

Synthesis and Characterization of Nonaqueous Deposited Nanocrystalline CdS Film

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Abstract— A nanocrystalline CdS film can be deposited by chemical bath deposition using non aqueous medium. XRD analysis confirms the crystalline structure of CdS (002) with 34 nm crystallite size. The as deposited films are stoichiometric in nature with Cd and S atomic % ratio equal to 1.0. The field emission scanning electron microscope and atomic force microscopy studies reveals a densely packed non porous granular deposit with RMS value of roughness equal to 92nm. The band gap of the film is measured by spectroscopy and it is observed to 2.40 eV which is in good agreement with the reported result. The photoluminescence prominent peak of the CdS film is observed to be 392 nm.

Keywords— CdS, characterization, Non Aqueous medium, Photoluminescence, XRD.

I. INTRODUCTION

Nanocrystalline cadmium sulphide (CdS) II-VI semiconducting material has direct band gap of 2.42 eV. Due to their wide applications in the field of optoelectronic devices, light emitting diode, solar cells, etc CdS II-VI semiconductor is most important [1]. Cadmium sulphide is used as a window layer in high-efficiency thin film solar cell based on CdTe or CuInSe₂ [2,3]. CdS gain much attention for preparation of quantum dots whose properties are much different than bulk due to their large surface to volume ratio and their reduced size. In CdS based solar cells, such as ZnS or CdZnS could lead to decrease in window absorption losses and improvements in the short circuit current of the cells [4, 5]. CdS thin films have been deposited by several techniques like vacuum evaporation, sputtering, electrodeposition, spray pyrolysis, chemical bath deposition (CBD), Laser ablation, etc [6-14]. Among all these techniques CBD is used because very simple instruments are required, low cost technique, for large area

deposition, no fumes are given out, etc in comparison to other methods.

Non-aqueous bath offer greater flexibility in choosing deposition sources, higher working temperature ranges and also free from the ubiquitous hydrogen evolution reaction. Hydrogen is often a nuisance in producing stress and pinhole deposits [15]. The main objective of the present work is to develop, the cadmium based binary II-VI compounds CdS thin films by using chemical bath deposition (CBD) technique in non-aqueous medium. In this paper, we report the deposition of good quality CdS thin film using ethylene glycol. We report the structural, surface morphology, composition and optical properties of as-deposited CdS films. The films were investigated by XRD, FESEM, EDS, AFM, UV-VIS spectrophotometer, FTIR and PL spectrophotometer.

II. MATERIALS AND METHODS

2.1 Synthesis of CdS thin films

The electrolyte was prepared by using AR grade 0.2M CdCl₂ dissolved in 40ml of ethylene glycol. The temperature of the electrolyte was maintained at 160°C. The electrolyte was aged for two hours. The deposition was carried out under continuous stirring. The molybdenum substrate of dimension 1.5cm×1cm×0.1cm were polished with 600 grit carborandum paper, thoroughly washed with soap solution, water and then with distilled water. The molybdenum substrate was dipped inside the electrolyte with the help of rigid support. After loading the sample 0.4M thiourea was introduced in the electrolyte. The electrolyte was stirred and deposited for 15 minutes. After the deposition of films the substrate was washed with distilled water for 15 seconds to remove counter ions and organic impurities.

2.2 Characterization

The crystallographic structure of as-deposited CdS film was analysed with a Bruker AXS Diffractometer model D8 using CuK α radiation with the wavelength 1.54Å. The average grain size in the as-deposited CdS films were obtained by using Debey-Scherrer formula. Surface morphology and composition of the CdS film was carried out using Field Emission Electron Microscope model Quanta 200F, FEI Netherland. An optical property was measured using UV-VIS spectrophotometer model Lambda-25 Perkin-Elmer with wavelength range of 300nm to 900nm. FTIR analysis was carried out using the spectrometer model-IR Prestige-21, Shimadzu within the wave number range of 500cm⁻¹ to 4500cm⁻¹. Photoluminescence studies were carried out using spectrophotometer model-RF 5301pc, Shimadzu with wavelength variation 300nm to 800nm.

III. RESULTS AND DISCUSSIONS

3.1 Structural characterization of the films

The X-ray diffraction pattern of CdS film is shown in figure1. The XRD pattern shows that the as-deposited nanocrystallineCdS thin film is polycrystalline in nature with a hexagonal structure. The strong diffraction peak is observed at $2\theta = 26.76^\circ$ which can be ascribed due to (002) reflection planes of the hexagonal CdS structure. Reflection due to molybdenum substrates are observed at planes (110), (220), and (211). The crystallite size of the CdS thin film is affected by deposition conditions. It is useful to obtain the information of the structural properties of the thin film by XRD measurement. The crystallite size D of the CdS thin films is determined from the (002) peak using the Scherrer formula [16].

$$D = K\lambda / \beta \cos\theta$$

Where, K= Constant equal to 0.94

λ = Wavelength of X-ray (=1.54Å)

β = Full width at half maxima of (002) peak in radian

θ = Diffracted angle

The average grain size of as-deposited CdS thin film prepared for 15 minutes is 34nm.

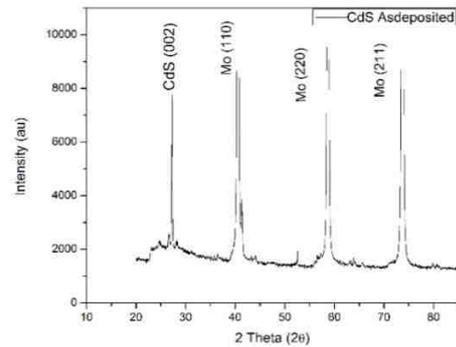


Fig.1: XRD analysis of as deposited CdS film.

3.2 Surface Morphology and Energy Dispersive Spectroscopy (EDS) Analysis

Fig.2. Shows the surface morphology of as-deposited CdS thin film deposited on molybdenum substrate. The FESEM photograph is taken at a magnification of 10,000X. From the micrographs, it is observed that the as-deposited CdS film is uniform, grains are distinct and in single state. The surface of the film is without any void, pinhole, crack, etc.

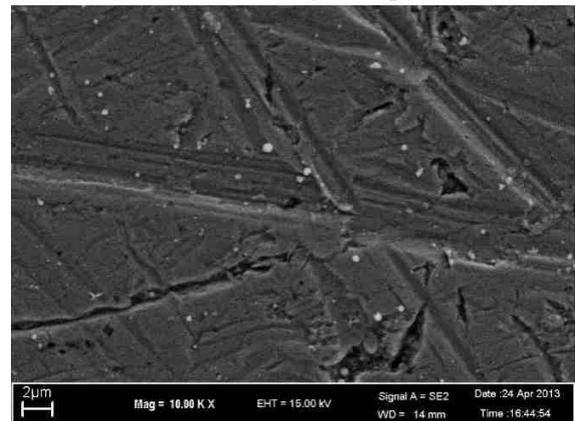


Fig.2: FESEM Photograph of as deposited CdS film

Table.1: Weight percentage and Atomic percentage of as-deposited CdS film.

CdS	Atomic %	Weight %
Cd	29.11	39.23
S	27.13	10.43
Mo	43.76	50.34

Fig.3. shows the chemical composition of as-deposited CdSnanocrystalline thin film. It is clear from spectra peaks that cadmium (Cd), sulphur(S) and molybdenum are

present. The peak of molybdenum is due to the substrate. In CdS film, the ratio of atomic percentage of Cd and S are observed to be nearly equal to 1.0. The atomic percentage and weight percentage of Cd and S are given in Table.1.

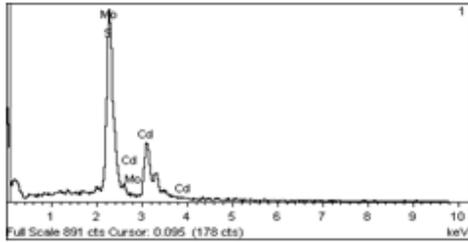


Fig.3: EDS analysis of as deposited CdS film

Fig. 4 and 5 shows the AFM photographs of as deposited CdS film in two dimension and three dimension respectively. The root mean square (RMS) roughness, grain size, and surface morphology of the film are studied. The films are observed to have smaller grains, uniform grain size and randomly oriented. The variation of the surface roughness are observed at different temperatures. The RMS roughness is observed to be 92 nm.

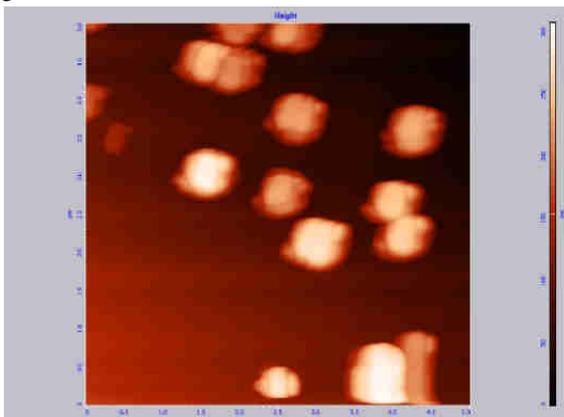


Fig.4: AFM analysis of as deposited CdS film in 2D

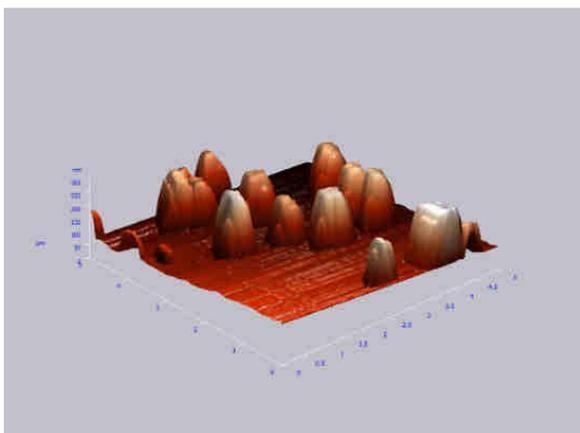


Fig.5: AFM analysis of as deposited CdS film in 3D

CdS is direct bandgap n –type semiconductor. According to Tauc’s relation, the absorption coefficient for direct bandgap is given by

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

Where, ‘ α ’ is the absorption coefficient ‘A’ is a constant, ‘ $h\nu$ ’ is the photon energy ‘ E_g ’ is the optical bandgap

Fig.6 shows the $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolation of the curve determines the optical bandgap (E_g) of CdS films. It is observed to be 2.40eV [17,18].

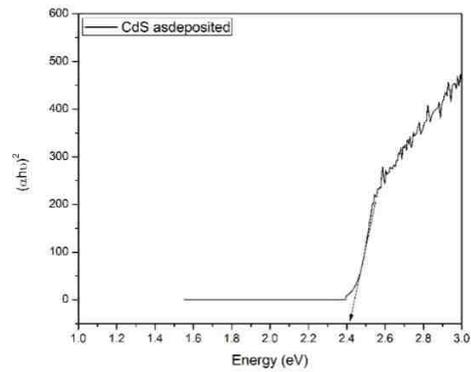


Fig.6: Graph between $(\alpha h\nu)^2$ versus $h\nu$ of as deposited CdS film

FTIR spectra of CdS nanoparticles is shown in fig.7. All the peaks in the spectra are identified. The IR frequencies as well as vibrational assignments for CdS nanoparticles are give in Table2. The peak appeared at 3450 cm^{-1} indicates the presence of O-H stretching due to the atmospheric moisture. The peak appeared at 1640 cm^{-1} is due to the vibrational mode of O-H bending. The peak at 2368 cm^{-1} is due to C-H group. The peak at 883 cm^{-1} indicates the bending vibration of C-H. The peak at 1180 cm^{-1} gives the C-O stretching vibration of absorbed ethylene glycol. The vibration absorption peak of the Cd-S peak is at 740 cm^{-1} [19, 20].

Table.2: IR frequencies and vibrational Assignments for CdS nanoparticle

Position(cm^{-1})	Assignments
3450	O-H Stretching
2386	C-H Stretching
1640	Bending Vibration of O-H
1180	C-O Stretching
883	Bending Vibration of C-H
740	Cd-S Stretching

Preliminary investigations show that photoluminescence (PL) spectra of the obtained CdS thin films have three distinct bands at 382nm, 495 nm and 676 nm, respectively. The measured photoluminescence excitation spectra corresponding to the two emission bands allows to fix the excitation wavelength at 300 nm suitable to the CdS thin films under consideration. The typical PL spectrum is presented in Fig.8. The chemical bath deposited CdS thin films reported in [4] has the PL band around 1.72 eV (the red band) due to sulfur vacancies, without the

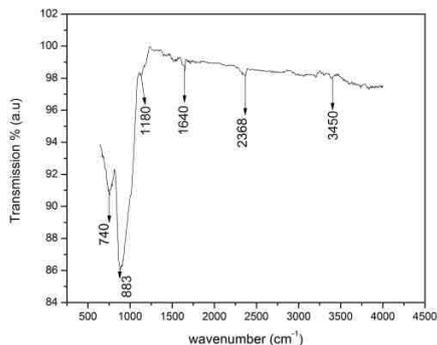


Fig.7: FTIR spectra of as deposited CdS film

corresponding exciton band. Yet, in any cases, the PL spectra of the CdS thin film under investigation have no red emission band. One might say that the obtained films are more or less stoichiometric. However, the Energy Dissipative X-ray (EDX) characterization is to be investigate for further detailed information in this regard.

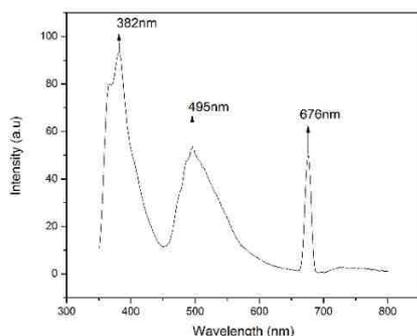


Fig.8: PL spectra of as deposited CdS film

IV. CONCLUSION

The CdS nanocrystalline thin film can be synthesis using non-aqueous medium. The structural, compositional, morphological and optical properties of the nano-film have been carried out. Hexagonal wurzite phase (002) of CdS film is observed with average grain size 34nm by scherrer

relation. The as deposited films are uniform, free from pin holes, voids, pits etc. FTIR spectra reveal the -OH stretching and bending. The presence of CH group is observed at 2368 cm^{-1} and the peak at 883 cm^{-1} indicates the bending vibration of C-H. The peak at 1180 cm^{-1} gives the C-O stretching vibration of absorbed ethylene glycol. Photoluminescence study shows spectra of the obtained CdS thin films have three distinct bands at 382nm, 495 nm and 676nm, respectively and the obtained films are more or less stoichiometric. Energy Dispersive Spectroscopy (EDS) shows the clear peaks of Cadmium (Cd), Sulphur(S) and molybdenum. The RMS roughness is observed to be 92 nm. In CdS film, the ratio of atomic percentage of Cd and S are observed to be nearly equal to 1.0.

REFERENCES

- [1] T Ohashi, K.Inaakoshi Y Hashimto, and K Ito, "Preparation of $\text{CuIn}(\text{SxSe}1-x)_2$ thin films by sulfurization and selenization" sol. Energy Mater. And solar cells, vol-50, page 37,1998.
- [2] A.Catalao, "Polycrystalline thin-film technologies: Status and prospects" solar Energy Mater. Solar cells vol 41/42 page-205,1996.
- [3] B.Dimmler, E.Gross, R.Meer, M.Powalla, D.Hariskos, M.Ruckh, U.Ruhle, H.W.Schock, proc. 25th IEEE photovoltaic specialists cof., Washington, DC, Page.757,1996.
- [4] R.B.Kale, C.D.Lokhade, "Influence of air annealing on the structural, morphological, optical and electrical properties of chemically deposited ZnSe thin films" Al. surf. Sci, vol 252, page 929, 2005.
- [5] J. Barman, J.P.Borah, K.C.Sarma, "Effect of ph variation on size and structure of cds nanocrystalline thin films "Chalcogenide Letters vol 5, (11), page 265, 2008.
- [6] J. Santamaria, I. Martil, E. Iborra, G. Gonzalez Diaz, F. Sanchez Quesada "Electrical characterization of all-sputtered CdS/CuInSe2 solar cell heterojunctions" solar cells, vol-28, page-31, 1990.
- [7] B.E. McCadless, A.Modal, R.W. Birkmire, "Galvanic deposition of cadmium sulfide thin films" Solar energy materials ad solar cells, vol 36, page 369,1995.
- [8] Steffe Preusser and Michael Cocivera, "Physical properties of electrodeposited cadmium sulfide" solar Energy Materials, vol 20, page 1,1990.
- [9] S.Yamaga, A. Yoshikawa, "Dependence of electrical and optical properties of iodine-doped cubic ZnCdS films on solid composition" J. Cryst Growth vol-117, page- 353,1992.

- [10] K.T.R.Reddy, P.J.Reddy."Studies of ZnxCd1-xS films and ZnxCd1-xS/CuGaSe2 heterojunction solar cells" J. physics D.Appl. phys.,vol 25,page 1345,1992.
- [11] M.E. Ozsa, D.R.Johnson, M.Sadeghi ad D.Sivapethasundarm, IEEE, (1994).
- [12] S.Kuraouchi, T. Nakazawa, A. Ashida, .Yamamoto, "Cadmium sulfide thin films prepared by chemical bath deposition method" Solar Energy Materials and Solar cells vol-35,page-185,1994.
- [13] S Keitoku, H Ezumi, H Osono, N Ohto,"Preparation of p-Type CdS Thin Film by Laser Ablation" Jpn J App phys vol-34, page-138, 1995.
- [14] B. Subrananian, C Sajeevviraju, M Jaya Chandra,"Brush plating of tin(II) selenide thin films" J cryst Growth, vol234,page-421,2002.
- [15] S.R.Kumar, R.B.Gore, S.K.Kulkarni, R.K.Pandey,"X-ray photoelectron spectroscopy and structure of the Cu-In alloy films" Thin solid Films, vol208, page-161, 1992.
- [16] Mahanty, S,Basak, D, Ruedu, F,Leon, M Journal of Electronic Materials, May1999.
- [17] T.Nakaishi, K,Ito,"Properties of chemical bath deposited CdS thin films" sol. Energy Mater. Sol. Cells. vol35, page-171, 1994.
- [18] P.P.Sahay, R.K.Nath and S.Tiwari,"Optical properties of thermally evaporated CdS thin films" Crystal. Res. Technology vol.42 (3),page- 275-280, 2007.
- [19] Silerstein, R.M.; Bassler, G.C.; and Morrill, T.C. "Spectrometric Identification of organic compounds." 4th ed. New York: John wiley and sons, 1981.
- [20] Nakanishi, Koji Infrared Absorption Spectroscopy. QD95.N383.